

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>E21B 43/02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/20129</b> <b>(43) International Publication Date:</b> 5 June 1997 (05.06.97)
<b>(21) International Application Number:</b> PCT/EP96/05374 <b>(22) International Filing Date:</b> 28 November 1996 (28.11.96) <b>(30) Priority Data:</b> 95203271.2 28 November 1995 (28.11.95) EP <b>(34) Countries for which the regional or international application was filed:</b> GB et al. <b>(71) Applicant (for all designated States except CA):</b> SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). <b>(71) Applicant (for CA only):</b> SHELL CANADA LIMITED [CA/CA]; 400 - 4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA). <b>(72) Inventors:</b> BOSSAERTS, Jan, Dirk; Volmerlaan 6, NL-2288 GD Rijswijk (NL). EIJDEN, Gerbrand, Jozef, Maria; Volmerlaan 6, NL-2288 GD Rijswijk (NL). <b>(74) Agent:</b> SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.; P.O. Box 302, NL-2501 CH The Hague (NL).		<b>(81) Designated States:</b> AU, CA, NO, NZ, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> METHOD OF TREATING AN UNDERGROUND FORMATION  <b>(57) Abstract</b>  A method of treating an underground formation comprising the sequential steps of: (a) contacting the formation with an aqueous medium; (b) contacting the formation with a hydrocarbon fluid; (c) contacting the formation with a solvent in the form of a glycol ether; and (d) contacting the formation with a consolidation solution of between 30 and 60 %m of monomeric and/or polymeric organic polyepoxides having more than one epoxy group per molecule and between 5 and 20 %m of a curing agent in the solvent.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

## METHOD OF TREATING AN UNDERGROUND FORMATION

The present invention relates to a method of treating an underground formation to improve its strength. The method is particularly suitable for treating an underground hydrocarbon-containing formation from which hydrocarbons can be produced. Such an underground hydrocarbon-containing formation is called a reservoir.

Production of hydrocarbons from such a reservoir is usually done through a well drilled from surface to the reservoir. Such a well is cased to prevent collapse of its wall. To facilitate fluids flowing into the well, the part of the well extending into or through the reservoir is either not cased or, when cased, the casing is perforated locally. If the underground formation includes sandstone, production of hydrocarbons may cause formation minerals such as sand to be loosened and to be entrained by the fluids flowing into the well, particularly after water break through. The entrained materials cause wear of production equipment through which the fluid passes, and it is expensive to separate and to dispose the material. To reduce the amount of entrained materials, the formation is strengthened using an epoxy resin system.

A particular problem is encountered when the underground formation includes 'dirty' sand, which is sand covered with contaminants such as hydrocarbon oil and water. The presence of these contaminants will adversely affect the bond between the sand particles and the epoxy resin and consequently the strength of the treated formation.

USA patent specification No. 3 481 403 discloses a method of treating an underground formation, which method

- 2 -

comprises contacting the underground formation with a solvent in the form of an alkyl ether of a C<sub>2</sub> to C<sub>6</sub> glycol containing at least one C<sub>1</sub> to C<sub>6</sub> alkyl group, and thereafter contacting the formation with a consolidation solution of an epoxy resin and a curing agent in a solvent of alcohol-kerosene. The solvent may be preceded by an oil preflush to remove water blocks. Moreover, if the formation has already produced large volumes of sand, a suspension of sand in water or oil can be injected before the treating starts to complement the lost sand.

It is an object of the present invention to improve the above described method, and it is a further object to provide a method for treating an underground formation a consolidation solution with a large concentration of epoxy resin can be used.

To this end the method of treating an underground formation according to the present invention comprises the sequential steps of:

- (a) contacting the formation with an aqueous medium;
- (b) contacting the formation with a hydrocarbon fluid;
- (c) contacting the formation with a solvent in the form of a mixture of glycol ethers; and
- (d) contacting the formation with a consolidation solution of between 30 and 60 %m (per cent by mass) of monomeric and/or polymeric organic polyepoxides having more than one epoxy group per molecule and between 5 and 20 %m of a curing agent in the solvent.

In the specification and the claims the term 'glycol ether' is used to refer to an ether of a C<sub>2</sub> to C<sub>6</sub> dihydric alcohol containing at least one C<sub>1</sub> to C<sub>6</sub> alkyl group, and the term 'epoxy resin' will be used to refer to monomeric and/or polymeric organic polyepoxides having more than one epoxy group per molecule.

In the method of the present invention, the formation is contacted with three pre-flushes which are injected

- 3 -

into the formation one after the other. The first pre-flush is an aqueous medium, the aqueous medium is injected into the formation to displace oil present in the pores of the formation away from the zone to be treated. The displacement of oil by the aqueous medium is an immiscible displacement, and consequently some oil will not be removed. The oil that is not removed is called connate oil. Thereafter the formation is contacted with a hydrocarbon fluid to displace water present in the pores away from the zone to be treated. Moreover, the hydrocarbon fluid will dissolve any connate oil that has not been removed by the aqueous medium. The displacement of water by the hydrocarbon oil is also an immiscible displacement, and consequently some water will not be removed. However, as the displacement of connate oil by the hydrocarbon oil is miscible, substantially all connate oil is removed. Subsequently the formation is contacted with the solvent in the form of the mixture of glycol ethers to displace the residual hydrocarbon fluids and water. As the mixture of glycol ethers is miscible with both hydrocarbons and water, the displacement is miscible and substantially no hydrocarbons or water will be left in the formation. The formation is fully saturated with the solvent.

After the formation has been treated in this way, the formation is contacted with the consolidation solution of between 30 and 60 %m of monomeric and/or polymeric organic polyepoxides having more than one epoxy group per molecule and between 5 and 20 %m of a curing agent in the solvent.

The present invention is based on the finding that solvent in the form of the mixture of glycol ethers provides miscible displacement of both water and oil, and that the solvent is an excellent solvent for the epoxy resin and the curing agent. The latter feature allows

- 4 -

contacting the formation with a concentrated consolidation solution of the epoxy resin, which consolidation solution has an acceptable viscosity. Moreover, as it is the same liquid as the liquid used in the last pre-flush, there are no compatibility problems.

The aqueous medium used in the first pre-flush may be a brine for example an aqueous solution of 2 %m of KCl.

To restore permeability, after the formation has been contacted with the consolidation solution of step (d) the formation is contacted with a viscosified hydrocarbon fluid, for example a mixture of aliphatic hydrocarbons. This so-called over-flush will displace the majority of the resin phase and restore permeability. The viscosity of the over-flush is larger than the viscosity of the hydrocarbon pre-flush.

The oil can be any hydrocarbon oil, such as diesel oil or crude oil.

Suitable glycol ethers for the solvent are mono ethers of the dihydric alcohols. Very suitable are the glycol ethers selected from the group including methoxypropanol, butoxyethanol, hexoxyethanol and the isomers of these glycol ethers.

To adjust the viscosity of the solvent, the solvent may further contain a minor amount, for example less than 10 %m, of a polyethylene glycol having an average molecular mass of about 400.

The invention will now be described in more detail with reference to the experiments.

To illustrate that the consolidation solution of solvent and combination of polyepoxides and curing agent is not viscous the viscosity of several consolidation solutions was determined in a CONTRAVES LS-30 Low Shear viscosimeter at a temperature of 25 °C. The epoxy resin used was EPIKOTE 828 (Trade Name, EPIKOTE 828 is obtained by reacting diphenylol-propane with epichlorohydrin, it

- 5 -

has a molecular mass of between 300 and 450), the curing agent used was methylene dianiline. The results for different consolidation solutions have been summarized in Table 1. The term 'solids content' is used to refer to the content of epoxy resin and curing agent.

Table 1. Viscosities in mPa.s of several consolidation solutions.

solvent	Solids content in %m				
	30	40	50	60	70
methoxypropanol	4.84	8.04	14.1	26.1	70.5
hexoxyethanol	10.5	20.5	29.0	58.4	110

To illustrate the effect of method of the present on the unconfined compression strength, several samples were made and subjected to two treatments, a treatment according to the invention and a treatment not according to the invention. For each test three samples were made of Nieuwe Pekela sand (grain diameters in the range of from 0.075 to 0.150 mm) in a glass tube, each sample had a diameter of 3.5 cm and a length of 17 cm. After the sand had been placed in the tube the porosity,  $\Phi$  (in %), was determined. The sand pack was flushed with butane to remove air, and thereafter the sand pack was flushed with an aliphatic hydrocarbon in which butane dissolves to remove the butane. Then the initial permeability,  $K_i$  (in Darcy), was determined.

To simulate formation conditions, the following fluids were injected: (1) methoxypropanol; (2) brine (2 %m KCl); and (3) about 10 pore volumes of crude oil to establish irreducible water saturation.

The samples were subjected to two treatments, a first one according to the invention, and a second one not according to the invention.

- 6 -

The treatment according to the invention comprises contacting the samples filled with crude oil at irreducible water saturation in the following sequence:

- 5 (a) contacting the sample with 2 pore volumes of a 2 %m KCl brine;
- (b) contacting the sample with 2 pore volumes of gasoil;
- (c) contacting the sample with 2 pore volumes of methoxypropanol;
- 10 (d) contacting the sample with 1 pore volume of a consolidation solution of EPIKOTE 828 (Trade Name) and methylene dianiline in methoxypropanol, the solids content being 60 %m; and
- (e) contacting the sample with 2 pore volumes of viscosified aliphatic hydrocarbons.

15 After the treatment the final permeability,  $K_e$  (in Darcy), and the unconfined compression strength, UCS (in bar), were determined. The results are summarized in Table 2.

Table 2. Results of the treatments according to the present invention.

	$\Phi$ in %	$K_i$ in D	$K_e$ in D	UCS in bar
Average	36.07	4.72	4.19	143

20 In the treatment not according to the invention, the steps (a), (b) and (c) have been omitted. Thus the samples with crude oil at irreducible water saturation were only treated in accordance with steps (d) and (e) of the above example.

25 After the treatment the final permeability,  $K_e$  (in Darcy), and the unconfined compression strength, UCS (in bar), were determined. The results are summarized in Table 3.



- 7 -

Table 3. Results of the treatments not according to the present invention.

	$\Phi$	$K_i$	$K_e$	UCS
	in %	in D	in D	in bar
Average	35.21	4.68	4.71	83

From the above data it can be concluded that the unconfined compression strength in the experiment with the method according to the present invention is larger than the unconfined compression strength with the method not according to the present invention.

C L A I M S

1. A method of treating an underground formation comprising the sequential steps of:
  - (a) contacting the formation with an aqueous medium;
  - (b) contacting the formation with a hydrocarbon fluid;
  - 5 (c) contacting the formation with a solvent in the form of a glycol ether; and
  - (d) contacting the formation with a consolidation solution of between 30 and 60 %m of monomeric and/or polymeric organic polyepoxides having more than one epoxy
  - 10 group per molecule and between 5 and 20 %m of a curing agent in the solvent.
2. Method according to claim 1, wherein the glycol ether is selected from the group including methoxypropanol, butoxyethanol, hexoxyethanol and the isomers of these
- 15 glycol ethers.
3. Method according to claim 1 or 2, further comprising the step of contacting the formation with a viscosified hydrocarbon fluid.

## INTERNATIONAL SEARCH REPORT

Inter Application No

PCT/EP 96/05374

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 E21B43/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 463 664 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 2 January 1992 see page 3, line 5 - line 8; claims 1,4 ---	1-3
Y	US 3 915 232 A (C. GRUESBECK) 28 October 1975 see column 2, line 66 - column 3, line 2 see column 2, line 12 - line 28 see column 5, line 27 - line 32 see column 8, line 55 - column 9, line 30 ---	1-3
A	US 3 481 403 A (J.L. GIDLEY) 2 December 1969 cited in the application see claims 1,9 --- -/--	1-3

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

24 March 1997

Date of mailing of the international search report

04. 04. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Hilgenga, K

# INTERNATIONAL SEARCH REPORT

Inter. Application No.  
PCN/EP 96/05374

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>GB 2 046 816 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V.) 19 November 1980 see page 9, line 55 - page 10, line 25 -----</p>	1-3

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/05374

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 463664 A	02-01-92	AU 630814 B	05-11-92
		AU 7822591 A	12-12-91
		CA 2043970 A	08-12-91
		DE 69103693 D	06-10-94
		DE 69103693 T	02-03-95
		RU 2015304 C	30-06-94
		US 5129458 A	14-07-92
-----			
US 3915232 A	28-10-75	CA 1027846 A	14-03-78
-----			
US 3481403 A	02-12-69	NONE	
-----			
GB 2046816 A	19-11-80	CA 1132783 A	05-10-82
		US 4291766 A	29-09-81
-----			